



DECLARATION

I, Chieko KOBAYASHI, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true, and faithful translation into English made by me of the of patent application No.2004-082144.

Signed this 6 of April, 2010

A handwritten signature in black ink, consisting of a stylized 'C' followed by a horizontal line and a vertical stroke, positioned above a solid horizontal line.

Chieko KOBAYASHI

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Application Number: 2004-082144

The country code and
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to be used for filing
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Convention, is

JP2004-082144

Applicant(s): SUMITOMO CHEMICAL COMPANY, LIMITED

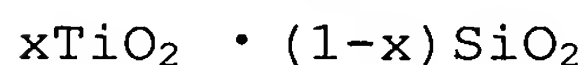
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[List of Documents]
 [Document name] Claims 1
 [Document name] Specification 1
 [Document name] Drawings 1
 [Document name] Abstract 1
 [Identification Number of general power of attorney]
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[Document Name] Scope of the claims for Patent

[claim 1]

A catalyst used for producing a propylene oxide by epoxidation reaction of propylene using peroxide to give the propylene oxide which has an X-ray diffraction pattern indicated below and which is a titanasilicate represented by the formula.



wherein x denotes a numerical value of 0.0001 to 0.1.

X-ray diffraction patterns

(Interplanar spacing of lattice $d/\text{\AA}$)

13.2 ± 0.6

12.3 ± 0.3

11.0 ± 0.3

9.0 ± 0.3

6.8 ± 0.3

3.9 ± 0.2

3.5 ± 0.1

3.4 ± 0.1

[claim 2]

The catalyst according to claim 1, wherein the peroxide is hydrogen peroxide.

[claim 3]

The catalyst according to claim 1 which is obtained by a catalyst production process not employing a calcination operation at the temperature of 200 °C or more.

[claim 4]

A method for producing a propylene oxide which comprises epoxidation reaction of propylene using peroxide in the presence of the catalyst according to one of claims 1 to 3 to give the propylene oxide.

[claim 5]

The method for producing a propylene oxide according to claim 4, wherein an alcohol is used as a solvent.

[claim 6]

The method for producing a propylene oxide according to claim 4, wherein tert-butanol is used as a solvent.

[Document Name] Specification

[Title of the Invention] Catalyst used for producing propylene oxide and method for producing propylene oxide

[TECHNICAL FIELD]

[0001]

The present invention relates to a catalyst used for producing a propylene oxide and a method for producing a propylene oxide. More specifically, the present invention relates a catalyst used for producing a propylene oxide by epoxidation reaction of propylene using a peroxide to give the propylene oxide, which has a catalytic activity equally to or more active than that of known catalyst and which can be prepared at an inexpensive price, without more complex processes, and a method for producing a propylene oxide using the catalyst.

[BACKGROUND ART]

[0002]

A technique for epoxidation reaction of propylene using a peroxide to produce propylene oxide is known (For example Patent document 1). As these known technique, a method using a Ti (titanium)-MWW catalyst for epoxidation reaction.

[0003]

However, the catalyst has had a problem in view of catalyst costs due to long and complicated processes to produce it.

[0004]

[Patent document 1] Japanese Unexamined Patent Publication No. 2003-327581

[DISCLOSURE OF THE INVENTION]

[Subject what the invention is to solve]

[0005]

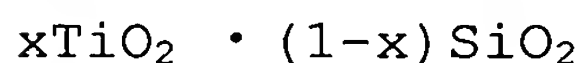
Under the circumstance, the subject what the invention is to solve is to provide a catalyst used for producing a propylene oxide by epoxidation reaction of propylene using peroxide to give the propylene oxide, which has a catalytic activity equally to or more active than that of known catalyst and which can be prepared at an inexpensive price, without more complex processes, and a method for producing a propylene oxide using the catalyst.

[Means for solving the problem]

[0006]

That is, the first invention of the present invention relates to a catalyst used for producing a propylene oxide by epoxidation reaction of propylene using peroxide to give the propylene oxide

which has an X-ray diffraction pattern indicated below and which is a titanasilicate represented by the formula.



wherein x denotes a numerical value of 0.0001 to 0.1.

X-ray diffraction patterns

(Interplanar spacing of lattice $d/\text{\AA}$)

13.2 ± 0.6

12.3 ± 0.3

11.0 ± 0.3

9.0 ± 0.3

6.8 ± 0.3

3.9 ± 0.2

3.5 ± 0.1

3.4 ± 0.1

The second invention of the present invention relates to method for producing a propylene oxide which comprises epoxidation reaction of propylene using peroxide in the presence of the catalyst according to one of claims 1 to 3 to give the propylene oxide.

[Effect of the invention]

[0007]

The present invention can provide a catalyst used for producing a propylene oxide by epoxidation reaction of propylene using oxide to give the propylene oxide, which has a catalytic activity equally to or more active than that of known catalyst and which can be prepared at an inexpensive price, without more complex processes, and a method for producing a propylene oxide using the catalyst.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0008]

The catalyst of the present invention shows X-ray diffraction patterns

(Interplanar spacing of lattice $d/\text{\AA}$)

13.2 ± 0.6

12.3 ± 0.3

11.0 ± 0.3

9.0 ± 0.3

6.8 ± 0.3

3.9 ± 0.2

3.5 ± 0.1

3.4 ± 0.1

These X-ray diffraction patterns can be measured by using a conventional X-ray diffractometer employing copper K- α radiation.

[0009]

The catalyst of the present invention has all of the above-mentioned X-ray diffraction patterns. In the present invention, typically, X-ray diffraction peak intensity denotes a local maximum value in the above-mentioned interplanar spacing of lattice, and may be found as a shoulder peak in the case where X-ray diffraction peaks of the catalyst of the present invention overlap each other.

[0010]

Among the above-mentioned X-ray diffraction patterns, a peak of $d=13.2 \pm 0.6$ Å is characteristic of the catalyst of the present invention. The peak of $d=13.2 \pm 0.6$ Å exists around 2θ (θ is Bragg angle) $=6.7^\circ$ in the case of using copper K- α radiation employed in a conventional X-ray diffractometer, and it is known that this peak is a peak derived from (002) lattice plane and specific to a layer structure of an MWW type layered precursor as described in 'Catalyst', 158, vol. 43, (2001).

[0011]

The catalyst of the present invention is a titanosilicate represented by the formula $x\text{TiO}_2 \cdot (1-x)\text{SiO}_2$ wherein x denotes a numerical value of 0.0001 to 0.1.

[0012]

The production method of the present invention will be explained.

[0013]

The examples of the method for producing the catalyst of the present invention include a method for producing a layered

precursor of Ti-MWW zeolite, as described in 'Chemistry Letters', 774-775, (2000), Japanese Unexamined Patent Publication No. 2003-32745 or 'Chemical Communication', 1026-1027, (2002). That is, in the first method, the Ti-MWW precursor is obtained by heating a mixture containing a structure directing agent, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water. The Ti-MWW precursor is generally used as a catalyst after removing the structure directing agent in the fine pores.

[0014]

In the second method, B (boron)-MWW precursor is obtained by heating a mixture containing a structure directing agent, a boron-containing compound, a silicon-containing compound and water, preferably removing the structure directing agent in the fine pores from the B (boron)-MWW precursor and then calcining it to obtain B (boron)-MWW. The obtained B (boron)-MWW is deboronized by acid and then a structure directing agent, a titanium-containing compound and water are added thereto and the mixture is heated to produce a Ti-MWW precursor. The Ti-MWW precursor is generally used as a catalyst after removing the structure directing agent in fine pores and drying.

[0015]

Examples of the structure directing agent include piperidine, hexamethyleneimine and the like. Examples of the titanium-containing compound include tetraalkyl orthotitanate such as tetra-n-butyl orthotitanate, titanium halide or the like. Examples of the boron-containing compound include boric acid and the like. Examples of the silicon-containing compound include tetraalkyl orthosilicate such as tetraethyl orthosilicate, fumed silica or the like.

[0016]

A mixture containing the structure directing agent, the titanium-containing compound, the boron-containing compound, the silicon-containing compound and water is heated at typically 100 °C to 200 °C. The heating temperature of the mixture is typically raised at a rate of 0.01 °C/minute to 2 °C/minute. The heating time is typically approximately 2 to 240 hours. A hydrothermal synthesis method to be performed

under autogenous pressure of the mixture is generally known as a heating method. The hydrothermal synthesis method is mostly conducted in a batch method but may be conducted in a flow method.

[0017]

As described in 'Soritu 45 Shunen Kinen Osaka Taikai Tokubetu Koen Shotai Koen Dai 33 Kai Sekiyu/Sekiyu Kagaku Toronkai Kouen youshi', 77, (2003), MWW zeolite as seed crystal or hydrofluoric acid can also be added to a mixture containing a structure directing agent, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water.

[0018]

As a method of treating a Ti-MWW precursor with acids such as nitric acid, sulfuric acid or the like there is a known method by removing the structure directing agent in the fine pores. The Ti-MWW precursor is treated with an acid, thereafter separated from the acid by filtration, washed with water if necessary, dried and used as a catalyst.

[0019]

In case of using Ti-MWW as a catalyst, the Ti-MWW precursor is dried and thereafter needs to be calcined sufficiently for crystallizing; however, calcination is not always necessary in the present invention, and sufficient calcination for crystallizing does not need to be performed even though calcination is performed. The sufficient calcination requires so excessive costs that it impairs the effect of the present invention. That is, the catalyst of the present invention can be produced at an inexpensive cost as compared with Ti-MWW by not being sufficiently calcinated at 200 °C or more.

[0020]

The drying temperature is generally 20 °C or more and less than 200 °C. Too higher drying temperature requires more energy costs for heating. Too lower drying temperature requires more costs because drying time is prolonged and resulted in lowered production efficiency.

[0021]

The following methods are known as a drying method: a method of heating by a drier, a method of drying by sending heated gas

and a method of drying by using a spray drier that can simultaneously dry and form particles of approximately 1 to 1000 μm . In case of using a spray drier, the inlet temperature of hot air occasionally exceeds 200 °C, which is necessary heat for vaporizing a liquid and does not deteriorate the effect of the present invention as long as the outlet temperature of hot air is less than 200 °C.

[0022]

In case of using the catalyst in a slurry reactor or a fluidized-bed reactor, a method of drying by using a spray drier is preferable because it can simultaneously form and dry it.

[0023]

As described in 'Zeoraito no Kagaku to Kogaku' (Kodansha Scientific Ltd., 10, (2000)), it is known that the interlayer is subject to dehydration condensation to form an MWW structure, namely, cause crystallization into an MWW structure by raising the temperature of drying than 200 °C and further retaining the higher temperature for a long time. This operation is called calcination and distinguished from drying. The occurrence of crystallization into an MWW structure by calcination can be confirmed by measuring an X-ray diffraction pattern, namely, obtaining an X-ray diffraction pattern as shown in FIG. 2 in the case of using copper K- α radiation. It can be confirmed that a peak in the proximity of $2\theta = 6.7^\circ$ derived from a interplanar spacing of lattice of $d = 13.2 \pm 0.6 \text{ \AA}$ disappears in the obtained X-ray diffraction pattern.

[0024]

This is called calcination, which is different from drying. This calcination is known as the most convenient method for crystallization from an MWW precursor into an MWW structure. That is, sufficient calcination of an MWW precursor allows the dehydration condensation of the interlayer of the MWW precursor, so that crystallization is promoted to form an MWW structure. It is described in Japanese Unexamined Patent Publication No. 2003-32745 that the calcination temperature is preferably 200 °C to 700 °C, most preferably 400 °C to 600 °C. The calcination time is generally approximately 1 to 100 hours. Lower calcination temperature allows energy per unit of time to be

decreased; however, longer calcination time becomes so necessary as to decrease production efficiency and thereby require excessive costs. Higher calcination temperature causes necessary energy to increase so that excessive costs are required.

[0025]

The catalyst of the present invention does not require crystallization from an MWW precursor into an MWW structure, so that sufficient calcination in producing the catalyst is unnecessary. In particular, the catalyst of the present invention is most suitably produced by the process of producing a catalyst without having calcination operations at 200 °C or more. That is, without employing the calcination operations at 200 °C or more the catalyst production cost is more inexpensive.

[0026]

As it is described in 'Catalyst & Catalysis', 158, vol. 43, (2001), the catalyst of the present invention is known to have the peak intensity of an X-ray diffraction pattern to be obtained varies greatly with the catalyst preparation conditions, and a peak of sharp and strong intensity is occasionally found, while as shown in FIG. 1 of the present invention only a weak and broad peak as compared with an MWW structure is occasionally found. To our surprise, however, the catalyst of the present invention can maintain high catalytic activity even when only a weak and broad peak is found.

[0027]

The catalyst of the present invention is a catalyst used for producing a propylene oxide by performing an epoxidation reaction of propylene with the use of peroxide.

[0028]

Examples of the peroxide include inorganic peroxide such as hydrogen peroxide or the like, and organic peroxide such as cumene hydroperoxide or the like. Among these, hydrogen peroxide is preferable for the ready availability of raw materials thereto.

[0029]

A description is made to the method for producing a propylene oxide comprising an epoxidation reaction of propylene with the

use of peroxide in the presence of a catalyst of the present invention.

[0030]

In the present invention, the reaction can also be conducted in the presence of a solvent. Examples of the solvent that may be used include water, an organic solvent, supercritical fluid and the like. Examples of the organic solvent include an alcohol such as tert-butanol or the like, a ketone compound such as acetone or the like, an ether compound such as methyl-tert-butyl ether or the like, an ester compound such as ethyl acetate or the like, a nitrile compound such as acetonitrile, propionitrile or the like, an aliphatic hydrocarbon such as n-heptane or the like, an aromatic hydrocarbons such as toluene, cumene or the like, a halogenated hydrocarbon such as 1,2-dichloroethane or the like, and various organic compounds. Examples of the supercritical fluid include carbon dioxide or the like. Preferred solvents include the alcohol solvent, and preferred alcohol solvents include tert-butanol.

[0031]

The catalyst used for the present invention can show particularly higher activity as compared with Ti-MWW catalyst when a solvent having such a big molecule as comprising 4 or more elements except hydrogen atom(s) is used.

[0032]

Examples of the method of supplying hydrogen peroxide used for the present invention include a method of supplying a hydrogen peroxide solution previously produced, or a method of supplying hydrogen peroxide synthesized in situ. Examples of the method of synthesizing hydrogen peroxide in situ include a method of synthesizing hydrogen peroxide by using a transition metal catalyst such as Pd, Au or the like for synthesizing hydrogen peroxide in situ from hydrogen and oxygen, which is supported on or mixed with the catalyst of the present invention.

[0033]

Examples of the method of supplying cumene hydroperoxide used for the present invention include a method of supplying cumene hydroperoxide obtained by oxidizing cumene with oxygen.

[0034]

An epoxidation reaction of propylene by the present invention is usually carried out at a reaction temperature typically from 0 to 150 °C and under a reaction pressure typically of from 0.1 to 20 MPa.

[0035]

Examples of the reaction method include a fixed-bed flow reaction method and a slurry reaction method.

[EXAMPLES]

[0036]

Next, the present invention is described by referring to examples.

Example 1

The present invention is described by way of examples. That is, gel comprising 9.1 kg of piperidine, 25.6 kg of pure water, 6.2 kg of boric acid, 0.54 kg of TBOT (tetra-n-butyl orthotitanate) and 4.5 kg of fumed silica (cab-o-sil M7D) was prepared in an autoclave at room temperature under an atmosphere of air while stirred, and aged for 1.5 hours and thereafter tightly closed. The gel was heated-up over 10 hours under stirring, and thereafter retained at a temperature of 170 °C for 168 hours to thereby obtain a suspension by hydrothermal synthesis. The obtained suspension was filtered and thereafter washed with water until the filtrate showed around pH 10. Next, the filter cake was dried at a temperature of 50 °C. to obtain white powder, which still contained water. 3.5 L of 13 wt % nitric acid was added to 350 g of the obtained powder and refluxed for 20 hours. Subsequently, the powder was filtered, washed with water to the proximity of neutrality and sufficiently dried at a temperature of 50 °C to obtain 98 g of white powder. With regard to this white powder, an X-ray diffraction pattern was measured by using an X-ray diffractometer employing copper K- α radiation to obtain the X-ray diffraction pattern shown in FIG. 1. It was confirmed that the powder was a Ti (titanium)-MWW precursor,

[0037]

Interplanar spacing of lattice

$2\theta / ^\circ$	$d/\text{\AA}$
6.82	13.0
7.23	12.2

7.97	11.1
9.78	9.0
12.9	6.8
22.7	3.9
25.2	3.5
26.2	3.4

[0038]

The reaction was performed by using this Ti (titanium)-MWW precursor catalyst. That is, 36% H_2O_2 aqueous solution, tert-butanol and pure water were mixed well to prepare a solution of H_2O_2 : 5 wt %, water: 47.5 wt %, tert-butanol: 47.5 wt %. 12 g of the prepared solution and 0.010 g of the pulverized Ti (titanium)-MWW precursor catalyst were put into a 50-ml stainless-steel autoclave. Next, the autoclave was transferred onto an ice bath, which was filled with 10 g of liquefied propylene and further pressurized up to 2 MPa-G with nitrogen. The autoclave was put in a block bath made of aluminum so that the internal temperature became 40 °C, and 5 minutes thereafter when the internal temperature rose up to approximately 35 °C was regarded as reaction initiation. 1 hour after the reaction initiation, the autoclave was taken out of a hot water bath to take a sample. The pressure in starting the sampling was 2.6 MPa-G. The analysis was conducted by using gas chromatography. As a result, propylene oxide production activity per unit catalyst weight was $0.781 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[0039]

Example 2

The reaction was conducted in a similar manner as in Example 1 by using the catalyst used in Example 1 except for using a solution, prepared by well mixing approximately 36 wt % aqueous H_2O_2 solution, acetonitrile and pure water to contain H_2O_2 : 5 wt %, water: 47.5 wt %, acetonitrile: 47.5 wt %. As a result, propylene oxide production activity per unit catalyst weight was $0.319 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[0040]

Comparative Example 1

The Ti (titanium)-MWW precursor used in Example 1 was fired at a temperature of 530 °C for 6 hours to obtain Ti

(titanium)-MWW catalyst powder. It was confirmed by measuring an X-ray diffraction pattern by using an X-ray diffractometer in a similar manner as in Example 1 that the obtained powder had an MWW structure (FIG. 2).

[0041]

Interplanar spacing of lattice

$2\theta / ^\circ$	$d/\text{\AA}$
7.24	12.2
8.02	11.0
9.94	8.9
12.9	6.8
22.8	3.9
25.2	3.5
26.2	3.4

[0042]

The catalyst evaluation test was conducted in a similar procedure as in Example 1 by using 0.010 g of the obtained Ti (titanium)-MWW catalyst and a solution prepared to composed of H_2O_2 : 5 wt %, water: 47.5 wt %, tert-butanol: 47.5 wt %. As a result, propylene oxide production activity per unit catalyst weight was $0.309 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[0043]

Comparative Example 2

The catalyst evaluation test was performed in the same manner as Example 2 except for using the Ti (titanium)-MWW catalyst used in Comparative Example 1. As a result, propylene oxide production activity per unit catalyst weight was $0.300 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[Brief Description of the Drawings]

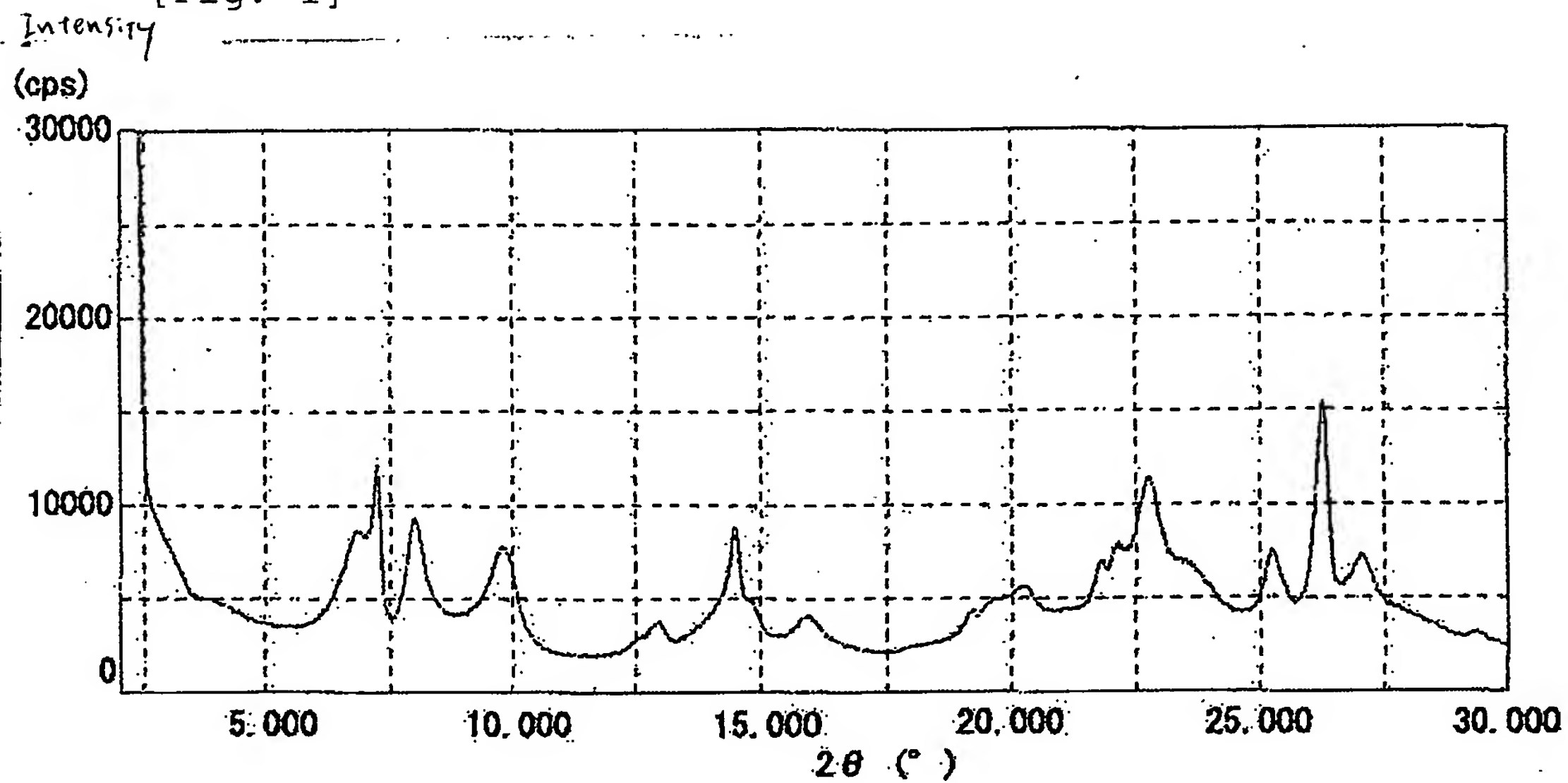
[0044]

[FIG. 1] FIG. 1 is a chart showing an X-ray diffraction pattern of a Ti (titanium)-MWW precursor catalyst used in Example 1.

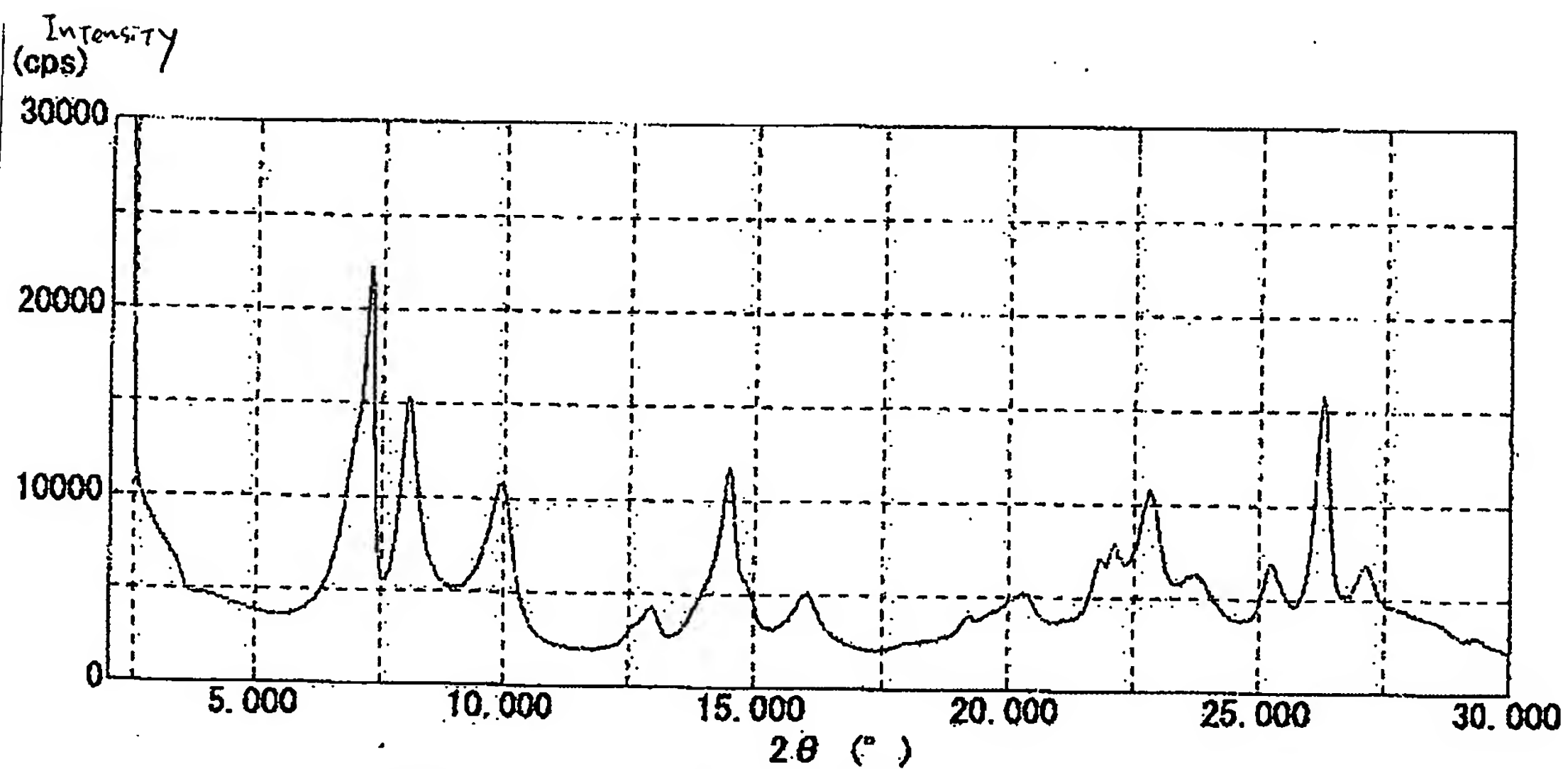
[FIG. 2] FIG. 2 is a chart showing an X-ray diffraction pattern of a Ti (titanium)-MWW catalyst used in Comparative Example 1.

[Document Name] Drawings

[Fig. 1]



[Fig. 2]



[Document name] Abstract

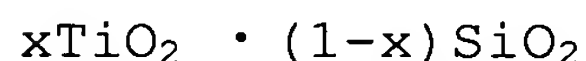
[Abstract]

[Problem]

To provide a catalyst used for producing a propylene oxide by epoxidation reaction of propylene using peroxide to give the propylene oxide, which has a catalytic activity equally to or more active than that of known catalyst and which can be prepared at an inexpensive price, without more complex processes, and a method for producing a propylene oxide using the catalyst.

[Means for solving the problem]

A catalyst used for producing a propylene oxide which has an X-ray diffraction pattern indicated below and which is a titanocilicate represented by the formula.



wherein x denotes a numerical value of 0.0001 to 0.1.

X-ray diffraction patterns

(Interplanar spacing of lattice $d/\text{\AA}$)

13.2±0.6

12.3±0.3

11.0±0.3

9.0±0.3

6.8±0.3

3.9±0.2

3.5±0.1

3.4±0.1

[Selective figure] Fig.1

Applicant Record

Identification No.:000002093

1. Date of changing registration: August 28, 1990
[reason for change] New Registration
Address: 5-33, Kitahama 4-chome, Chuo-Ku, Osaka
Name: SUMITOMO CHEMICAL INDUSTRIES, LIMITED

2. Date of changing registration: October 1, 2004
[reason for change] change of name
change of address
Address: 27-1, Shinkawa 2-chome, Chuo-ku, Tokyo
Name: SUMITOMO CHEMICAL COMPANY, LIMITED

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